PROCESS DEVELOPMENT AND SCALE UP OF ADVANCED ACTIVE BATTERY MATERIALS

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Project ID: ES167

Wednesday, June 8, 2016
Washington, D.C.

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2017
- Percent complete: on going

Budget

- Total project funding:
  - $1.2M in FY15
  - $1.2M in FY16

    $500K for Flame Spray Pyrolysis

    $300K for 10 L Taylor Vortex Reactor

Barriers

- Cost: Reduce manufacturing costs with advanced processing methods
- Performance: Synthesis route selection and process optimization for maximum performance

Partners

- Active material process R&D:
  - Argonne's Applied R&D Group
    - Material synthesis and scale-up
  - University of Illinois at Chicago
    - 3D elemental mapping
  - Technische Universität Braunschweig
    - Particle stress study
  - A123
    - Cathode precursor micronization
  - PPG Industries
    - Cathode material customization
  - SiNode Systems
    - Si-graphene composite synthesis
  - Cabot
    - Flame spray pyrolysis
  - Swiss Federal Institute of Technology
    - Flame spray pyrolysis

Objectives - Relevance

- The objective of this program is to provide a systematic engineering research approach to:
  - Develop ***cost-effective*** processes for the scale-up of advanced battery materials.
  - Provide ***sufficient quantities*** of these materials produced under rigorous quality control specifications for industrial evaluation of further research.
  - Evaluate ***material purity profiles*** and their influence on battery performance.
  - Evaluate ***emerging manufacturing technologies*** for the production of these materials.

- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing.
    - Reducing the risk associated with the commercialization of new battery materials.
  - This program provides large quantities of materials with consistent quality.
    - For industrial validation in large format prototype cells.
    - For further research on advanced materials.

Milestones

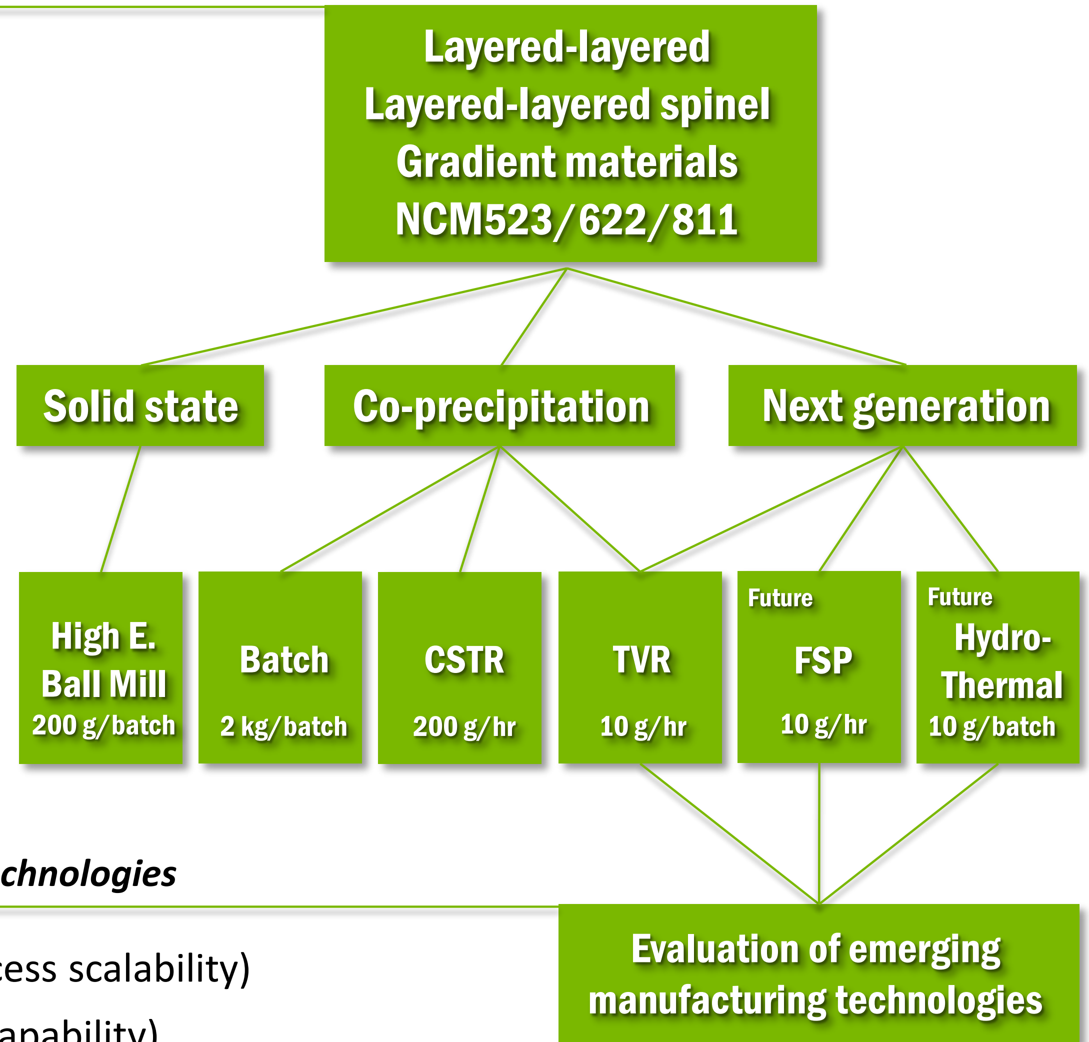
FY15	R&D	Layered-layered material – Kilogram production	*Completed*	15-Jun
	R&D	Layered-layered-spinel material – Evaluate the effect of spinel content	*Completed*	15-Aug
	R&D	Gradient material – Identify target composition	*Completed*	15-Jul
		– Complete preliminary assessment	*Completed*	15-Sep
		– Complete precursor optimization (NCM811 as Core composition)	*Completed*	16-Feb
FY16		– Preliminary synthesis of Core-Gradient material	*Completed*	16-Mar
		– Kilogram production of Core-Gradient material	Ongoing	16-Q2
		– Optimize the synthesis of Surface composition	Target	16-Q3
		– Optimize the thickness of Gradient layer	Target	16-Q4
		– Kilogram production of optimized Core-Gradient material	Target	17-Q1
		– Core-Shell material synthesis for comparison	Target	17-Q1
	Ind.	Spray drying – Micronization of nano-size LFP material	*Completed*	16-Mar
		– Reactive spray drying for Si-graphene composite	Ongoing	16-Q2
	R&D	FSP* set-up – Process basic design and installation	Ongoing	16-Q2
		– Identify target composition and produce preliminary material	Target	16-Q4
	Both	TVR** scale-up – 1 L TVR NCM material synthesis for electrodeposition R&D	*Completed*	16-Feb
		– 10 & 40 L TVR installation	Ongoing	16-Q3
		– Begin scale-up research using 1, 10 and 40 L TVRs	Target	16-Q4

* Flame Spray Pyrolysis ** Taylor Vortex Reactor

Approach - Strategy

Material Synthesis with Process R&D

- ❑ Define target active material
  - Evaluate bench-scale samples
- ❑ Select synthesis process and synthesis route
  - Batch, CSTR, TVR, FSP
  - Carbonate and hydroxide
- ❑ Produce intermediate material
  - 10 gram scale
  - Preliminary synthesis
  - Material evaluation
- ❑ Synthesis condition optimization by DoE
- ❑ Production and distribution
  - 1 ~ 10 kilogram scale
  - Assist other DOE programs



Evaluation of Emerging Manufacturing Technologies

- ❑ Taylor Vortex Reactor (evaluate process scalability)
- ❑ Flame spray pyrolysis (establishing capability)
- ❑ Hydrothermal synthesis (future)

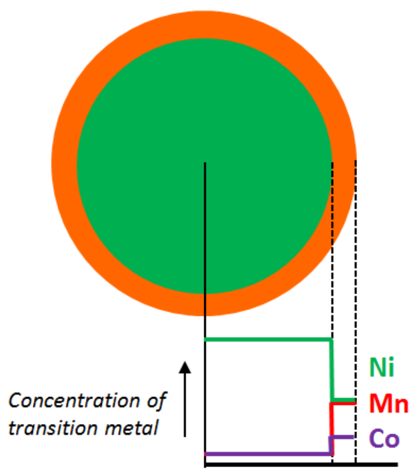
Gradient Material

- Gradient material will have the best of Core and Surface compositions

Core composition	-	Ni-rich material : high capacity, low stability
Gradient layer	-	Gradient layer : prevents the crack and segregation between Core and Shell
Surface composition	-	Mn-rich material : low capacity, high stability

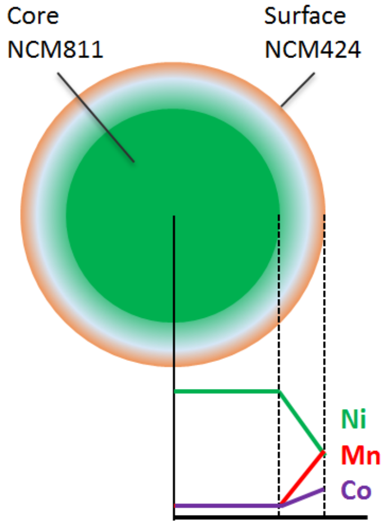
Core-Shell

- Low particle strength



High capacity
Low particle strength
Low stability

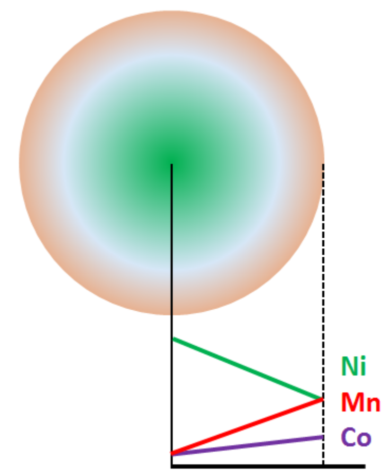
Core-Gradient (FY16)



Medium capacity
Medium particle strength
Medium stability

Full Concentration-Gradient

- Low capacity due to smaller Ni portion



Low capacity
High particle strength
High stability

1. To increase Ni portion for higher capacity
2. To optimize Core composition without internal porosity
3. To prepare small Core particle with better particle strength

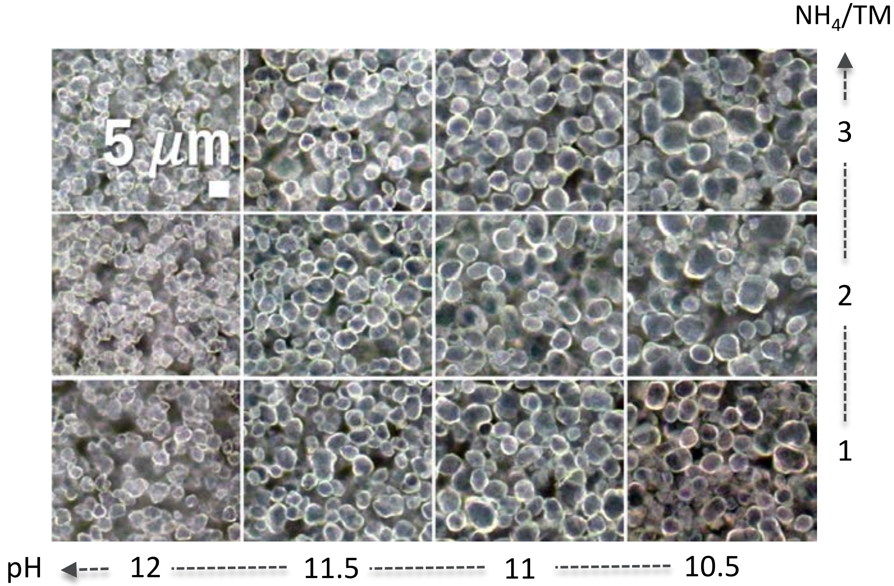
Synthesis optimization of Core NCM811 by DoE

Gradient Material

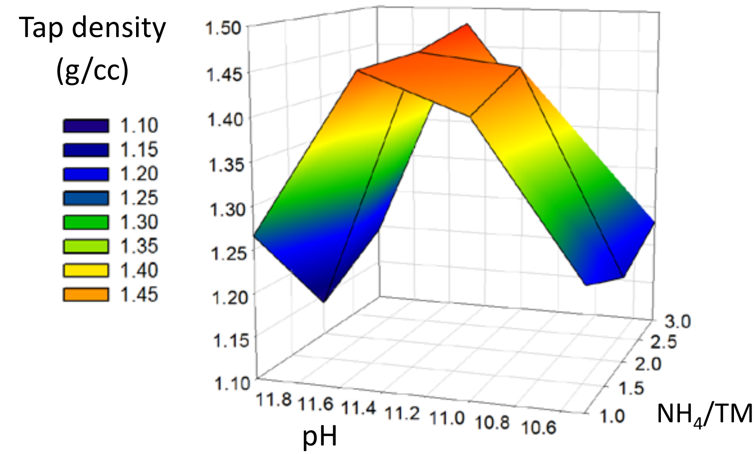
❑ Precursor optimization for Core NCM811

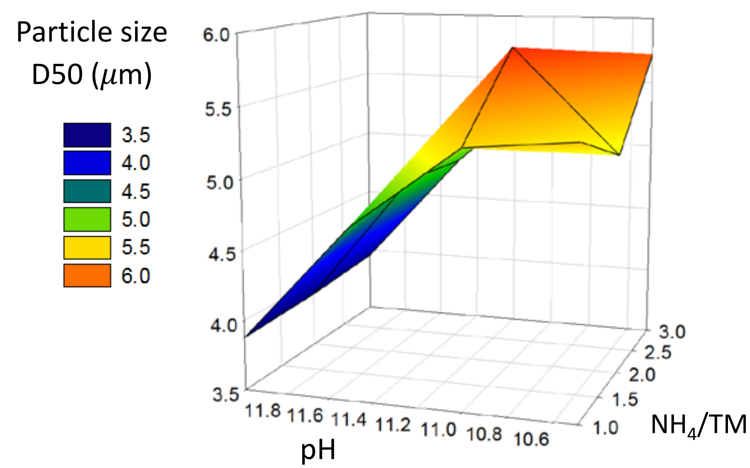
- <u>5μm</u> Core NCM811 : <u>Not commercially available</u>
- Dense particle
- Spherical morphology
- Narrow particle size distribution

– DoE: Multilevel Factorial Design
– 12-time 20 hr co-precipitations using 20 L Batch reactor



❑ 3D mesh plot for 12 precursors

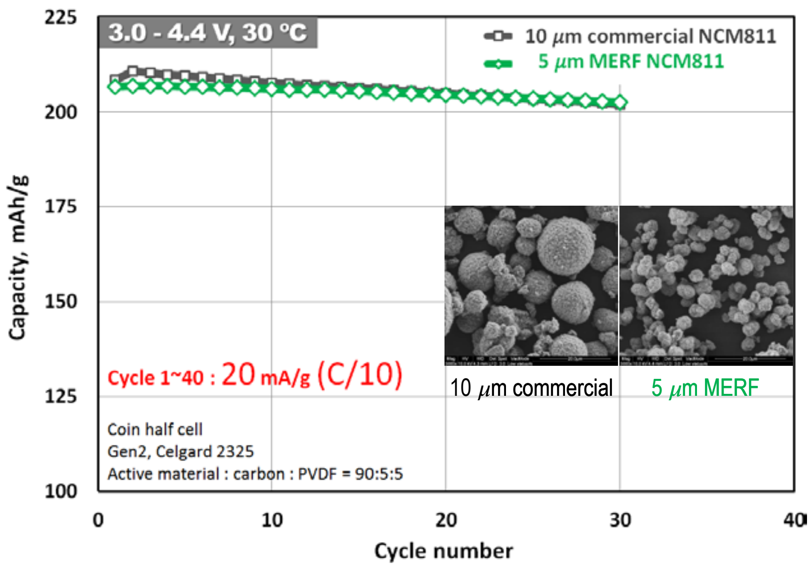


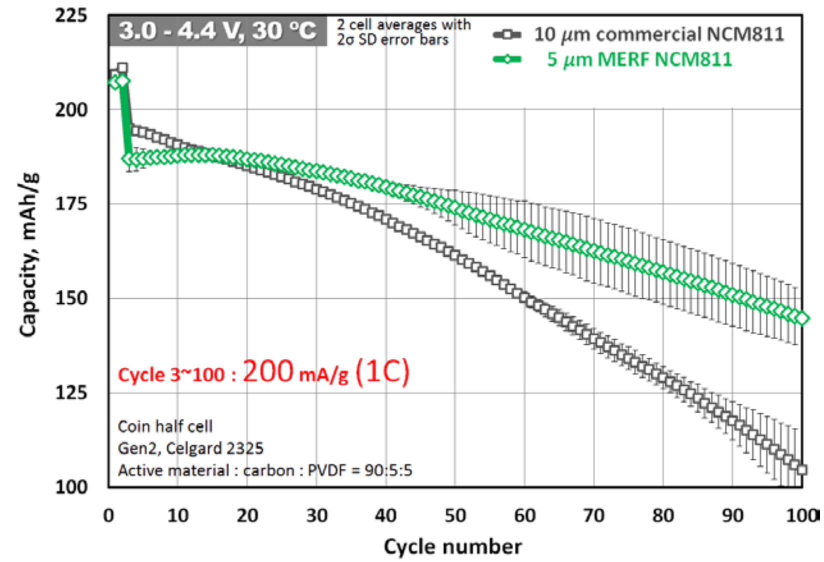


✓ *pH 11.5 shows 5 μm dense spherical particles.*
✓ *pH = 11.5 & NH4/TM = 2 condition was selected to prepare Core NCM811 at MERF.*

Gradient Material

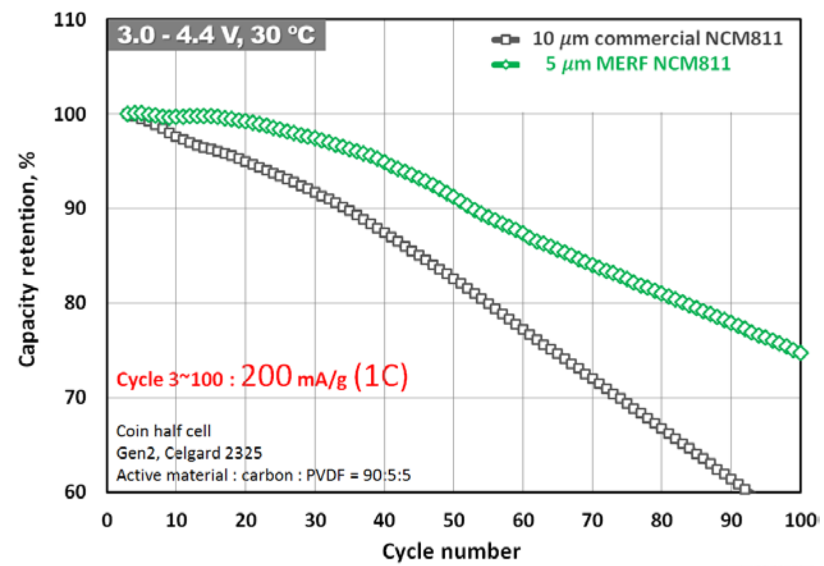
- Comparison between optimized MERF NCM811 and commercial NCM811





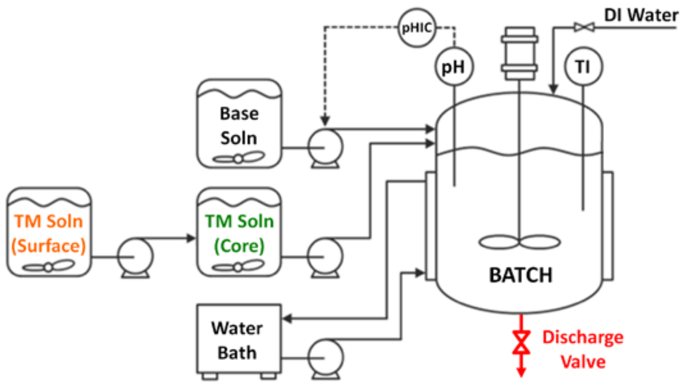
- *Quality of 5 μm Core NCM811 was verified.*
- *Both NCM811s show ~210 mAh/g.*
- *50g MERF NCM811 was sent to Technische Universität Braunschweig / CAMP for particle stress study.*

➡ *Synthesis of Core-Gradient material was started.*



Gradient Material

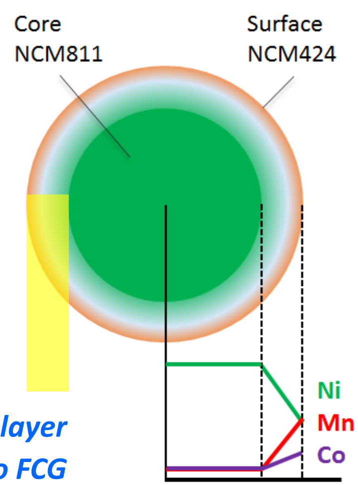
❑ Synthesis of Core-Gradient materials



* First, Core TM solution feeding to batch reactor
Then, Surface TM solution feeding to Core TM solution tank

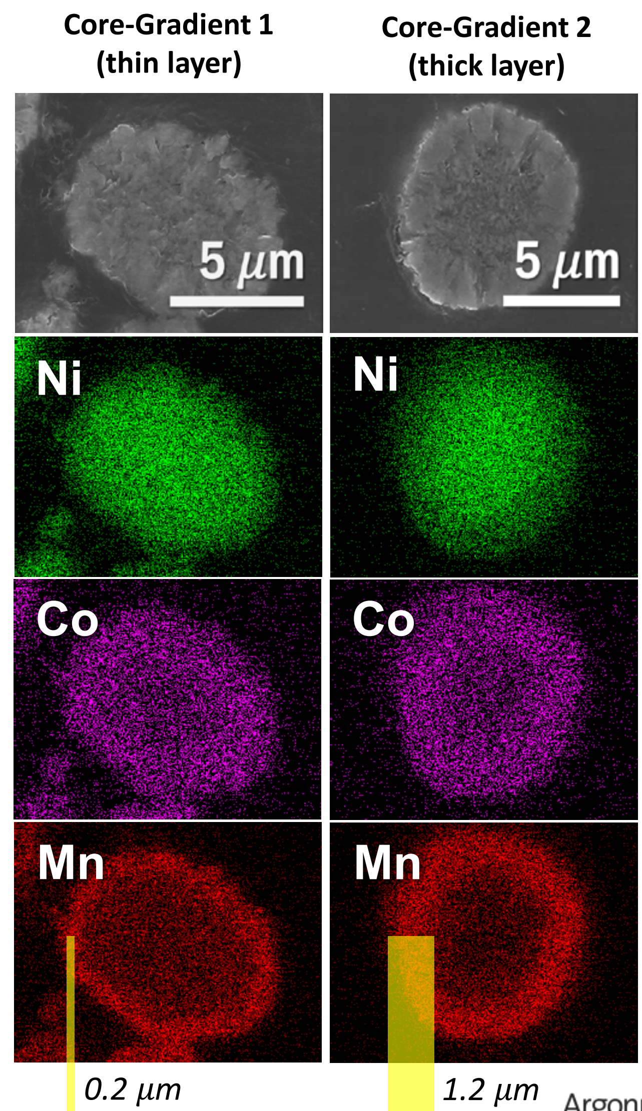
➡ Core TM solution changes to Surface TM solution gradually

■ 2 Core-Gradient materials were prepared to evaluate the effect of Gradient layer thickness



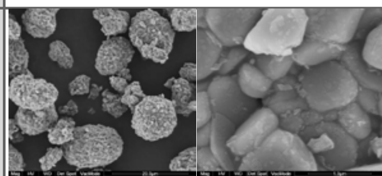
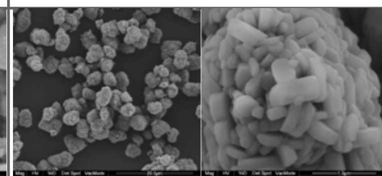
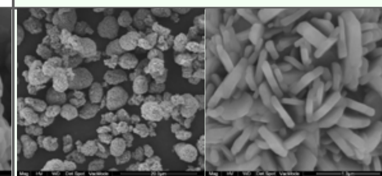
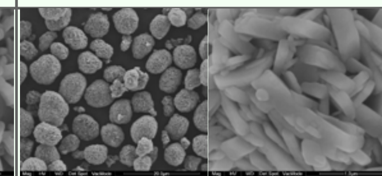
Thickness control of Gradient layer from normal NCM811 to FCG

❑ Elemental mappings



Gradient Material

❑ Comparison of prepared materials

Material	NCM622	NCM811 (no layer)	Core-Gradient 1 (thin layer)	Core-Gradient 2 (thick layer)
Scale / status	Commercial product	MERF pre-pilot Optimized	MERF pre-pilot Preliminary	MERF pre-pilot Preliminary
SEM 3,000x 50,000x				
Composition	NCM622	NCM811	~ NCM622	~ NCM523
ICP-MS analysis	$Li_{1.04}Ni_{0.60}Co_{0.20}Mn_{0.20}O_y$	$Li_{1.00}Ni_{0.77}Co_{0.12}Mn_{0.12}O_y$	$Li_{1.07}Ni_{0.57}Co_{0.17}Mn_{0.26}O_y$	$Li_{1.1}Ni_{0.46}Co_{0.19}Mn_{0.35}O_y$
Particle size D_{50} [µm]	**11.3**	**4.7**	**5.1**	**7.0**
Tap density [g/cc]	2.3	1.7	1.8	2.5
BET [m^2/g]	0.34	0.77	1.56	Ongoing
* FCE [%]	90.5	92.1	93.1	93.2
* Initial discharge capacity [mAh/g]	**188**	**207**	**185**	**178**

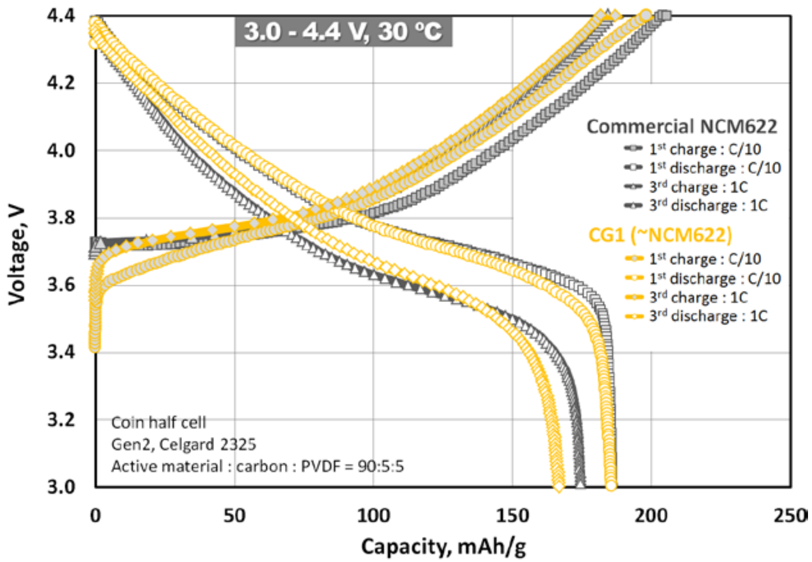
* At C/10, 3.0 – 4.4 V and 30˚C

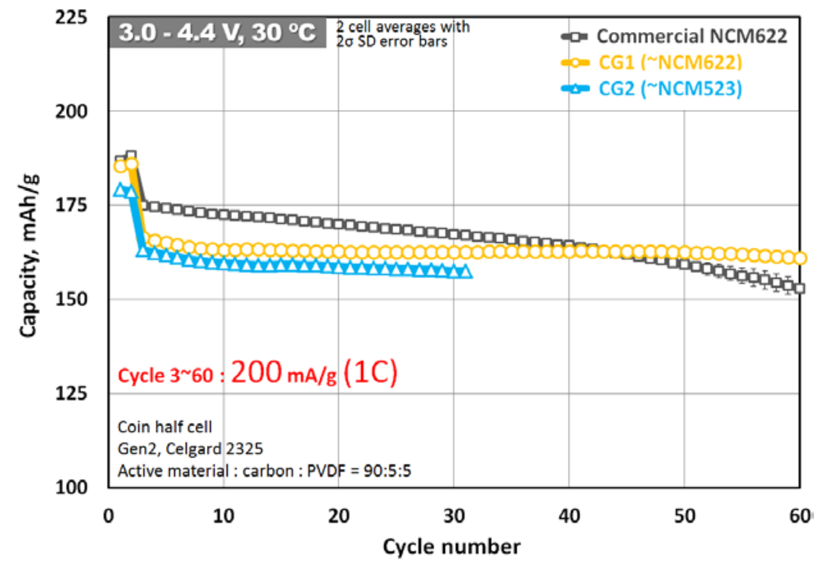
✓ *Core-Gradient materials have smaller primary particles and higher surface area than commercial NCM622.*

✓ *Core-Gradient 1 shows similar overall composition and discharge capacity compared to commercial NCM622.*

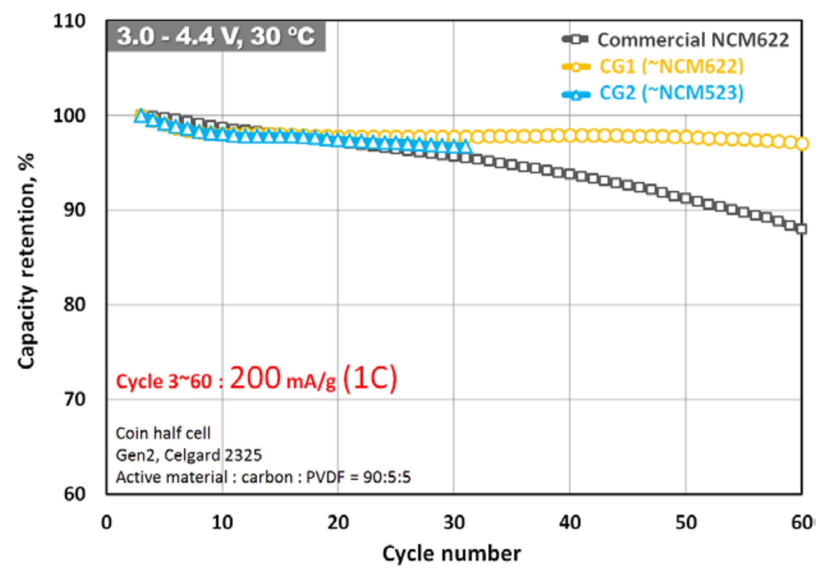
Gradient Material

❑ Comparison of electrochemical performance for 3 materials





- ✓ *CG1 shows lower capacity than commercial NCM622 at 1C. Gradient layer need to be optimized for better conductivity.*
- ✓ *CG1 shows superior capacity retention at high C-rate.*
- ✓ *CG2 (thick layer) needs further improvement.*
- ✓ *Core-Gradient structure has the best of Core (high capacity) and Surface (high stability) compositions.*



For further improvement :

1. Optimize the synthesis of Surface composition
2. Optimize the thickness of Gradient layer to determine trade-off between Core-Gradient and Full Concentration-Gradient

LL 1kg Scale-up and LLS Synthesis

- Layered-layered material, 1 kg

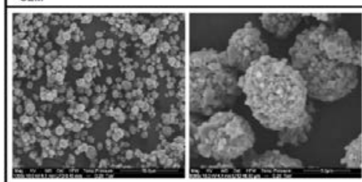
The Materials Engineering Research Facility (MERF), 370, ES, 9700 South Cass Avenue, Argonne, IL 60439
Gregory K. Krumdick(630-252-3952, gkrumdick@anl.gov), Youngho Shin(630-252-4861, yshin@anl.gov)

Outgoing Inspection Data Sheet	Sender	Receiver	Manager
	Youngho Shin	Stephen E. Trask	

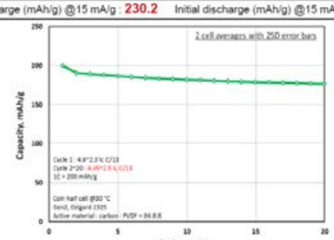
Target Cathode Composition	Prepared by	Lot Number	Weight	Delivery date
$Li_{1.03}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$	Youngho Shin Ozge F. Feridun	ES20150514	50 g	7/1/2015

Analysis		Results	Target	Judgement	Note	Method
Particle Size Distribution	D10 (μm)	5.2				Particle Size Analyzer
	D50 (μm)	9.9				
	D90 (μm)	18.8				
Specific Surface Area (m²/g)		0.83				BET
Tap Density (g/cc)		1.93				Tap Density Meter
Element mol %	Li / (Ni+Mn+Co)	1.03				ICP-MASS
	Ni / (Ni+Mn+Co)	0.61				
	Mn / (Ni+Mn+Co)	0.33				
	Co / (Ni+Mn+Co)	0.06				
For Use		Lithium Ion Secondary Battery				

SEM | Remark



Coin Cell Test : Initial charge (mAh/g) @15 mA/g : 230.2 Initial discharge (mAh/g) @15 mA/g : 200.1



ANL-ES-001(11/29/2011) Argonne National Laboratory Energy Systems Division

✓ *Total 61 g provided to CAMP and R&D group.*

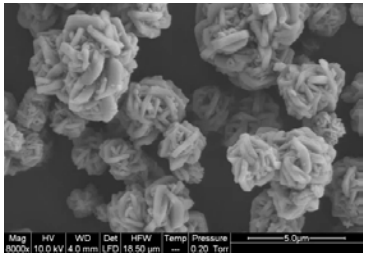
✓ *960 g available for the HE-HV program.*

ES253; Enabling High-Energy/Voltage Lithium-Ion Cells for Transportation Applications: Materials

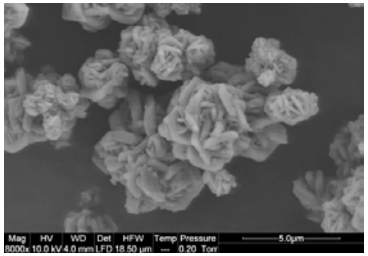
- Collaboration with M. Thackeray's group
  - Stabilizing spinel component incorporated into 'layered-layered' structure.
  - Layered-layered-spinel' system shows improved:
    - Capacity
    - Rate performance
    - First-cycle efficiency

- Synthesized LLS materials at MERF to optimize spinel content

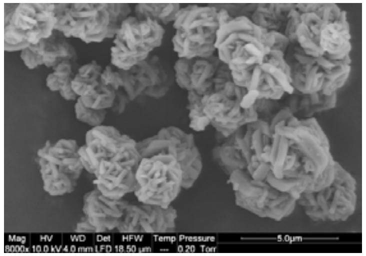
2% spinel
$Li_{1.236}Ni_{0.273}Mn_{0.536}Co_{0.191}O_y$



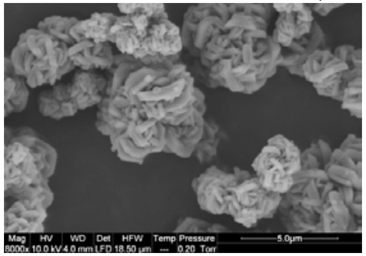
5% spinel
$Li_{1.210}Ni_{0.273}Mn_{0.536}Co_{0.191}O_y$



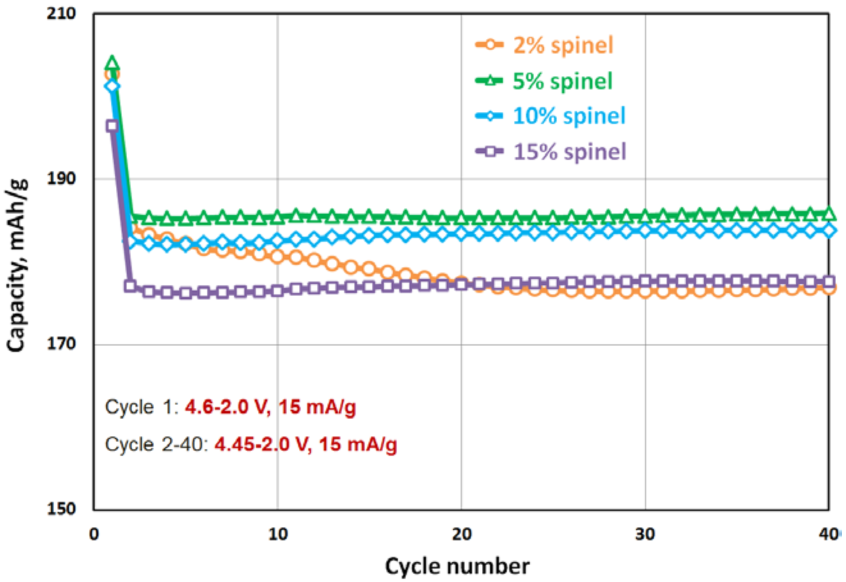
10% spinel
$Li_{1.176}Ni_{0.274}Mn_{0.536}Co_{0.190}O_y$

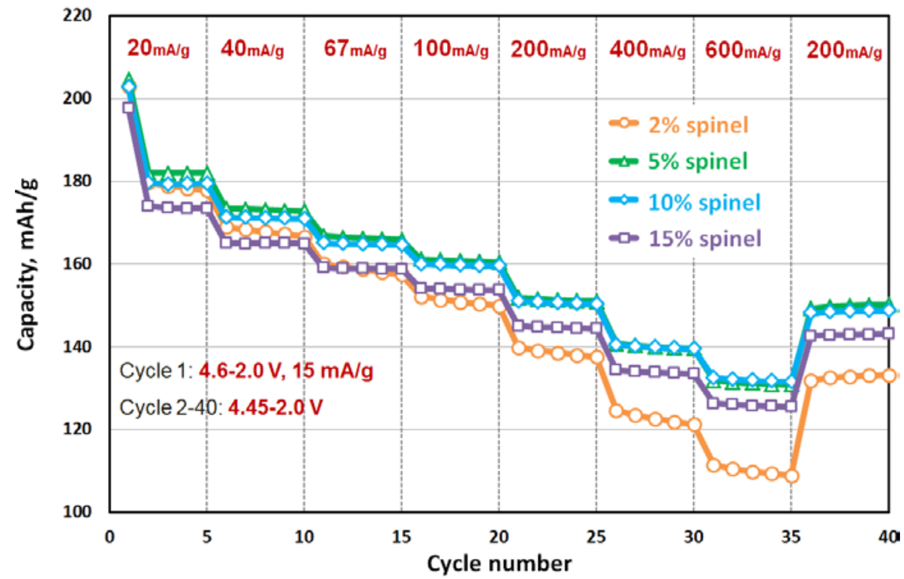


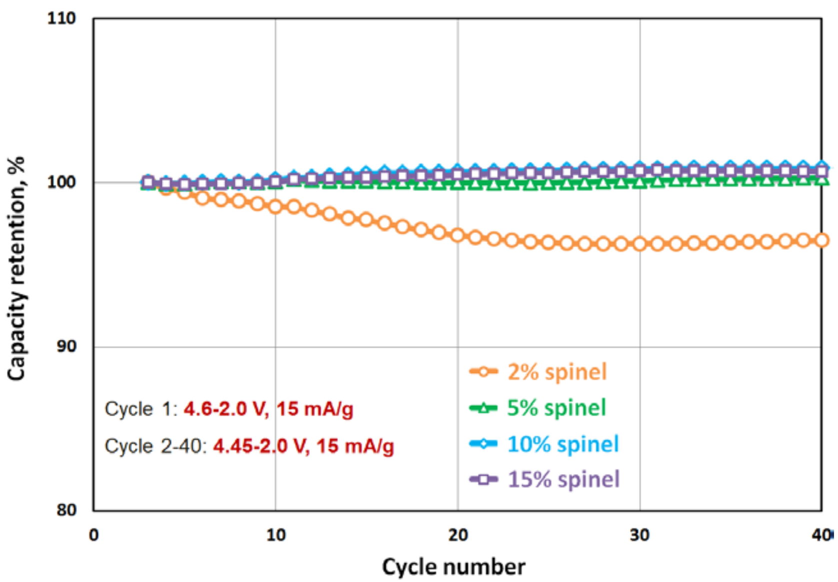
15% spinel
$Li_{1.135}Ni_{0.273}Mn_{0.536}Co_{0.191}O_y$



Electrochemical Performance of LLS Materials







- *5~10% spinel content shows higher discharge capacity.*
- *Spinel content more than 10% lowers the capacity.*
- *Spinel content more than 5% shows improved stability.*
- *Higher spinel content shows better rate capability.*

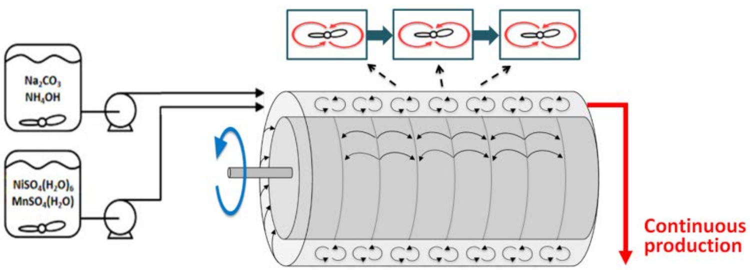
Effect of spinel content was clearly shown to collaborators for their further basic research.

ES049; Tailoring Spinel Electrodes for High Capacity, High Voltage Cells

TVR: NCM Synthesis and Process Scale-up

Laminar

❑ Taylor Vortex Reactor



– **TVR provides a homogeneous intense micro-mixing zone and produces spherical precursors with narrow size distribution.**

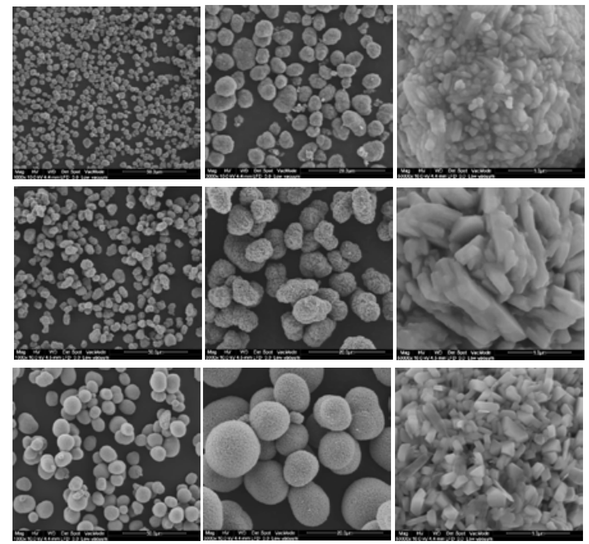
- Simplified operation
- Product uniformity
- Shorter residence time

❑ NCM materials from 1 L TVR

NCM523

NCM622

NCM811



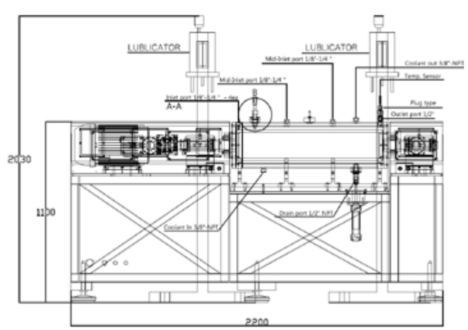
NCM523: Tap density = 2.1 g/cc; D50 = 5 µm; BET = 0.56 m^2/g

NCM622: Tap density = 2.0 g/cc; D50 = 8 µm; BET = 0.59 m^2/g

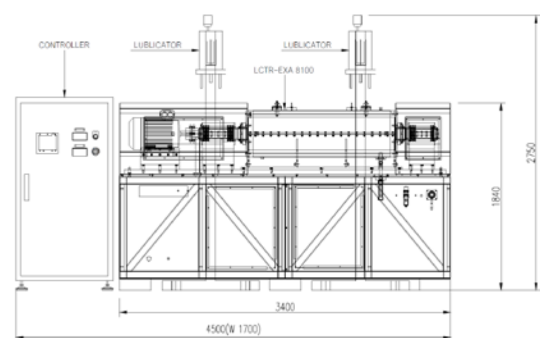
NCM811: Tap density = 2.4 g/cc; D50 = 14 µm; BET = 0.66 m^2/g

❑ Collaboration with equipment manufacturer to evaluate process scalability

1 L TVR in place



10 L TVR ongoing

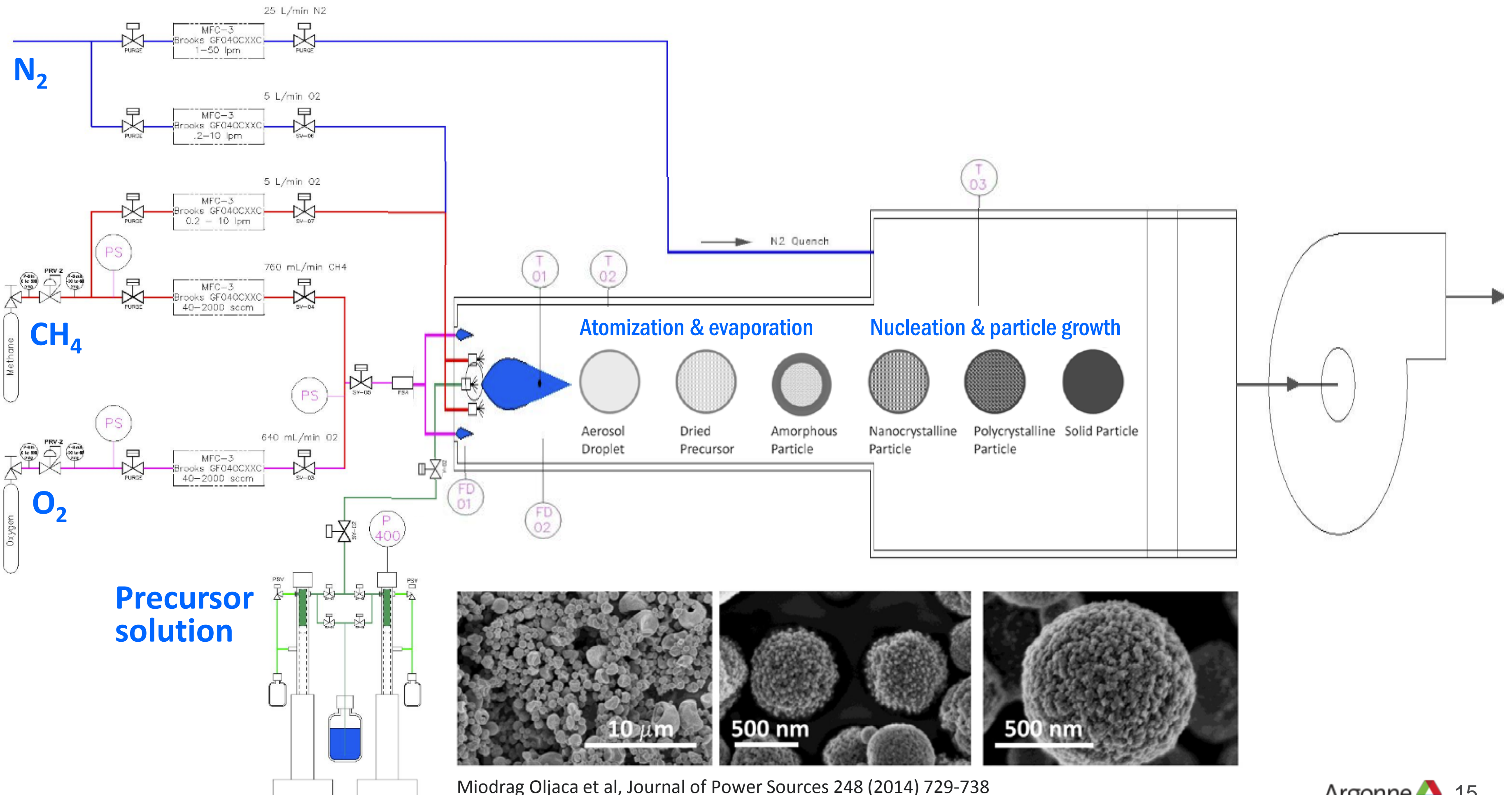


40 L TVR ongoing

Technical Accomplishments

FSP: Nano-material synthesis

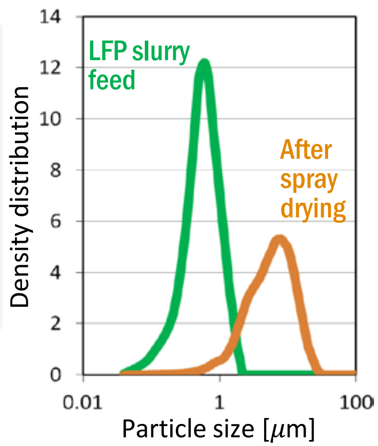
- Combustion of precursor aerosol solution w/o organic content
  - A system to produce nano-size active battery materials using a combustion flame spray unit
  - In collaboration with Miki Oljaca at Cabot Corp. and Sotiris Pratsinis at Swiss Federal Institute of Technology
  - Production rate target : 100 g/day



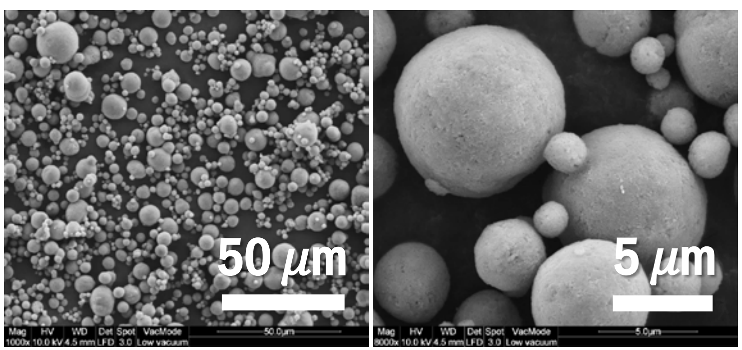
Miodrag Oljaca et al, Journal of Power Sources 248 (2014) 729-738

Spray Drying Application with Industry

- Spray drying of nano-size LFP slurry for micronization (A123)



- Water evaporation: 3 kg/hr
- Inlet air temperature: 250˚C
- Production rate: ~ 1 kg/hr



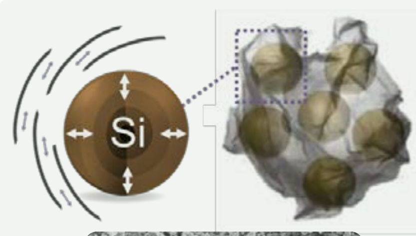
✓ *Particle size was increased from 500 nm to 5.6 μm.*

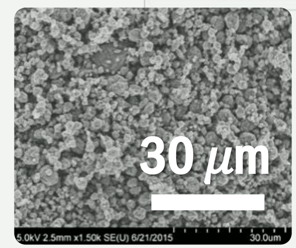
✓ *4.2 kg product was delivered to A123.*

A123 SYSTEMS

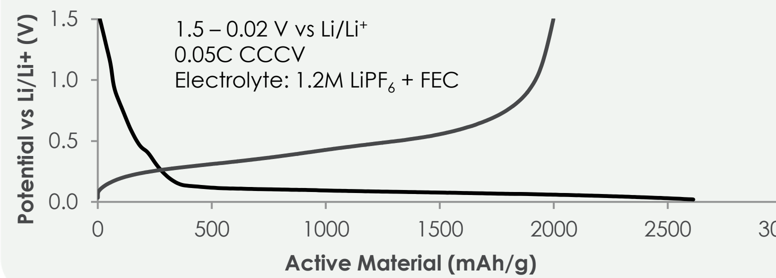
- Reactive spray drying for Si-graphene composite (SiNode)

SiNode SYSTEMS





Particle Size	0.5 – 2.0 μm
Real Density	2.3 g/cc
Specific Capacity	1800 - 2000 mAh/g
Volumetric Capacity	1000 – 1200 mAh/cc
Areal Loading	2.0 – 4.0 mAh/cm^2



✓ *Scale Si-graphene composite to Kg quantity.*

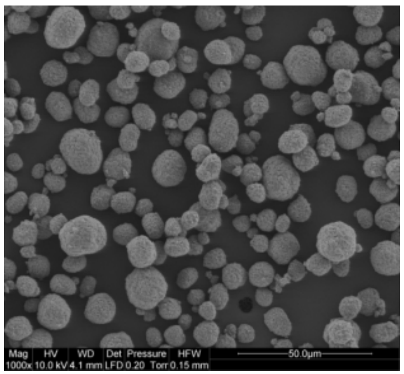
✓ *Control particle size and distribution.*

ES240; High Energy Anode Material Development for Li-Ion Batteries

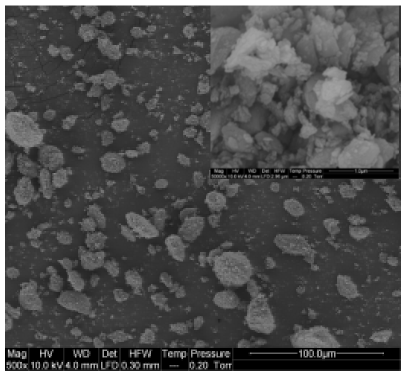
Active Material Synthesis with Tailored Properties

- MERF CRADA activity
  - Active materials proof of concept for compatibility with PPG's e-coat system
    - Prepare size-controlled NCM523

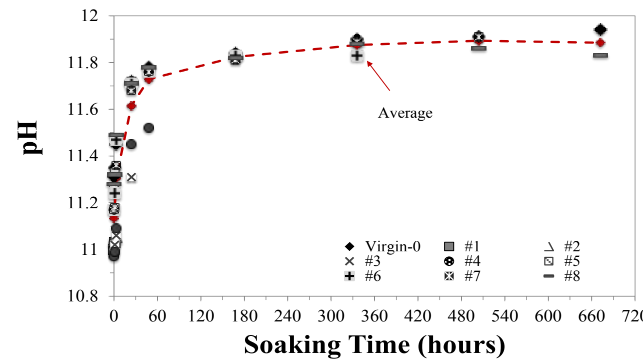
Pristine NCM 523



Ball milled sample (in IPA)



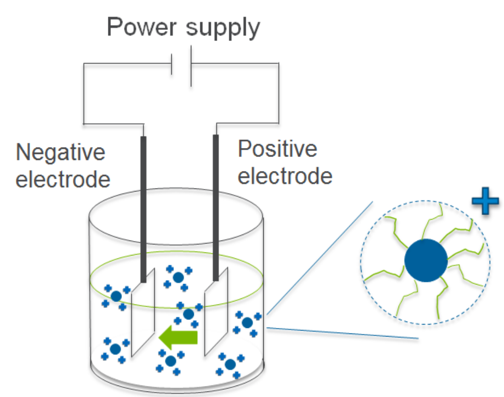
- Lithium dissolution
- Transition metal dissolution
- Monitor pH for particle suspension stability



- Custom cathode synthesis for DOE funded Electrodeposition for Low Cost Water Based Electrode Manufacturing project

Electrophoretic deposition :

- Charged monodispersed particles migrate to oppositely charged Al-foil.
- Requires small particle size (5µm and below) to obtain stable suspension in water-based baths.



ES263; Electrodeposition for Low-Cost, Water-Based Electrode Manufacturing

Responses to Previous Year Reviewers' Comments

THIS PROJECT WAS NOT REVIEWED LAST YEAR

Collaborations

- Active materials process R&D:
  - Argonne National Lab (HE/HV program)
    - Material Synthesis
  - Argonne National Lab (Michael Thackeray)
    - Material synthesis
  - PPG Industries - CRADA (Stuart Hellring)
    - Custom cathode materials
  - Cabot Corporation – (Miki Oljaca)
    - Flame spray pyrolysis
  - Technische Universitat Braunschweig (Wolfgang Haselrieder)
    - Particle stress evaluation
  - Laminar Co., Ltd – CRADA
    - Process scalability evaluation
  - Oak Ridge National Lab (Claus Daniel)
    - Custom material for R2R collaboration
  - Swiss Federal Institute of Technology (Sotiris Pratsinis)
    - Flame spray pyrolysis

- Materials provided :
  - University of Illinois at Chicago (Prof. Jordi Cabana)
  - NanoResearch Inc. (David Noye)
  - A123 Systems, Johnson Matthey, PPG
  - Argonne National Lab (various researchers)
  - Technische Universitat Braunschweig

- Electrochemical evaluation of scaled materials:
  - Argonne's Materials Screening Group (Wenquan Lu)
  - Argonne's CAMP facility (Andrew Jansen, Bryant Polzin, Steve Trask)

Open to working with any group developing advanced active materials that will be beneficial for the ABR program.

Remaining Challenges and Barriers

- New battery materials are continually being discovered and developed.
- There is a strong demand from the research community for high quality experimental materials in quantities exceeding bench scale synthesis.
- Production of high performance active materials is extremely complex. A detailed understanding of how process variables effect performance is critical to fully understand material cost and capability.
- Emerging manufacturing technologies need to be evaluated to further reduce production costs and increase performance of battery materials.
- Development and scale-up of material engineering technology like surface coating is challenging but has great promise to improve the performance of battery materials.

Proposed Future Work

- **Continue work on Gradient material (Core NCM811 + Surface NCM424)**
  - Kilogram scale-up of preliminary Core-Gradient material
  - Optimize the synthesis of Surface composition
  - Optimize the thickness of Gradient layer from normal NCM811 to FCG
  - Kilogram scale-up of optimized Core-Gradient material
  - Core-Shell and Full Concentration-Gradient material synthesis for comparison
  - Pouch cell evaluation of prepared materials

- **Active material engineering**
  - Complete reactive spray drying synthesis of Si-graphene composite (SiNode)
  - Synthesize custom material for electrophoretic deposition (PPG)
  - Synthesize custom material for AMO R2R program

- **Evaluate emerging manufacturing technologies**
  - Investigate process scalability with Taylor Vortex Reactors
  - Design and construction of FSP system and material synthesis

Summary

- **Layered-layered material**
  - Material synthesis at kilogram quantity and delivery have been completed
- **Layered-layered spinel material**
  - 5~10% spinel content shows improved capacity, rate performance and stability
- **Gradient material (Core NCM811 + Surface NCM424)**
  - Core 5 μm NCM811 was optimized by DoE.
  - 2 Core-Gradient materials were prepared and analyzed by elemental mapping
  - Core-Gradient material shows valid capacity and improved stability
- **Material Engineering with Industry**
  - 4.2 kg production of 5.6 μm powder from nano-size LFP slurry by spray dryer
  - Synthesis of sized-controlled NCM523 for electrophoretic deposition by 1 L TVR
- **Installation of 10 L & 40 L TVRs is ongoing**
- **Design and construction of FSP system is ongoing**

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- Swiss Federal Institute of Technology
  - Sotiris Pratsinis

Technical Backup Slides

Material Delivery to R&D Group and Industry

FY	Date	Material	Method	To	Purpose
15	06/19/2015	$Li_{1.03}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$	CSTR	ANL- CSE Division	HE/HV program
	07/01/2015	$Li_{1.03}Ni_{0.61}Mn_{0.33}Co_{0.06}O_y$	CSTR	ANL- CAMP	HE/HV program
	07/01/2015	$Li_{1.07}Ni_{0.60}Mn_{0.34}Co_{0.06}O_y$	TVR	ANL- CSE Division	HE/HV program
	09/22/2015	$Li_{1.14}Ni_{0.28}Mn_{0.53}Co_{0.19}O_y$	CSTR	ANL- CSE Division / Johnson Matthey	HE/HV program
	10/13/2015	$Li_{1.38}Mn_{0.67}Ni_{0.33}O_y$	CSTR	NanoResearch Inc.	Binder free electrode manufacturing
	10/15/2015	$LiNi_{0.50}Mn_{0.30}Co_{0.20}O_y$	Commercial + high temperature heat treatment	ANL- CAMP	Li_2CO_3 removal
	12/10/2015	$Ni_{0.60}Co_{0.20}Mn_{0.20}(OH)_2$	TVR	ANL- CSE Division	Wet surface coating
16	02/04/2016	$FePO_4$	Spray Dryer	A123	Drying optimization
	02/19/2016	$Li_{1.01}Ni_{0.80}Mn_{0.10}Co_{0.10}O_y$	CSTR	ANL- CAMP	HE/HV program
	03/04/2016	$Li_{1.02}Ni_{0.48}Mn_{0.31}Co_{0.21}O_y$	TVR	ANL- CAMP	PPG project
	03/07/2016	$Li_{1.01}Ni_{0.48}Mn_{0.31}Co_{0.21}O_y$	TVR + Water treatment	ANL- CAMP	PPG project
	03/08/2016	$Li_{1.01}Ni_{0.51}Mn_{0.29}Co_{0.20}O_y$	Commercial A + Water treatment	ANL- CAMP	PPG project
	03/17/2016	$Li_{1.07}Ni_{0.47}Mn_{0.34}Co_{0.19}O_y$	Commercial B + Water treatment	ANL- CAMP	PPG project
	03/18/2016	$LiNi_{0.80}Mn_{0.10}Co_{0.10}O_y$	TVR	ANL- CAMP	HE/HV program
	04/15/2016	$LiNi_{0.80}Mn_{0.10}Co_{0.10}O_y$	CSTR	Technische Universität Braunschweig / CAMP	Mechanical testing
	04/15/2016	$Li_{1.02}Ni_{0.48}Mn_{0.31}Co_{0.21}O_y$	TVR	Technische Universität Braunschweig / CAMP	Mechanical testing
	TBD	$Li_{1.02}Ni_{0.60}Mn_{0.20}Co_{0.20}O_y$	TVR	Technische Universität Braunschweig / CAMP	Mechanical testing
	TBD	$Li_{1.02}Ni_{0.80}Mn_{0.10}Co_{0.10}O_y$	TVR	Technische Universität Braunschweig / CAMP	Mechanical testing
	TBD	Core-Gradient	CSTR	UIC	Material advance characterization